

# How glasses explore configuration space

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We review a statistical picture of the glassy state derived from the analysis of the off-equilibrium fluctuation-dissipation relations. We define an ultra-long time limit where “one time quantities” are close to equilibrium while response and correlation can still display aging.

In this limit it is possible to relate the fluctuation-response relation to static breaking of ergodicity. The resulting picture suggests that even far from that limit, the fluctuation-dissipation ratio relates to the rate of growth of the configurational entropy with free-energy density.

## I. INTRODUCTION

Glassy systems spend long times out of equilibrium, i.e. in regions of configuration space which have vanishing Boltzmann probability. The evolution towards more and more optimized regions of phase space is so slow, that the fast degrees of freedom react on short time scales as if they were in equilibrium in the frozen background of the slow variables. On longer time scales however the off-equilibrium nature of the glassy phase shows up in the phenomenon of aging: the response to small perturbations, as well as the correlation functions, depend on the “age” of the glass, i.e. the time spent in the low temperature phase [1,2]. The dynamics becomes slower and slower as the age becomes larger and nevertheless, even on the largest scales observed there is no tendency to stop: the system eventually wanders away from any finite region of phase space.

In the last years, following some developments of spin glass mean field theory [3–5], many theoretical [6], numerical [7] and more recently experimental papers [8–10] have focused on the study of off-equilibrium fluctuation-dissipation relations. In [11], it has been shown that the fluctuation-dissipation relation found in mean-field analysis of glassy relaxation can be used to define effective temperatures, higher then the one of the heat bath governing the heat exchanges between slow degrees of freedom.

The analysis of the fluctuation-dissipation relation has revealed deep relations between aging dynamics and the nature of the free-energy landscape [12]. In this paper we would like to review a picture of glassy dynamics based on the analysis of these relations [13].

Two kinds of glassy systems emerge from experimental and theoretical analysis. One can identify two kind of glassy behaviors

- A first class, of which spin glasses are an example, where the asymptotic value of extensive quantities, like internal energy, and magnetization seem not to depend on the cooling rate or other differences in the cooling procedure.
- A second class, the one of structural glasses, in which the apparent asymptotic value of these quantities depends strongly on the cooling rate, and remain strongly different from the equilibrium values for the the largest time scales which can be probed.

Aging phenomena are common to both families. During aging the linear response to external perturbations displays age dependent behavior and anomalies with respect to equilibrium, which is conform to the fluctuation-dissipation theorem. Many efforts have been devoted to relate these anomalies to the properties of the underlying energy -or free-energy- landscapes [14,12,13,15–17].

A first step towards the comprehension of this relation can be achieved idealizing the first situation assuming that for long times *all* extensive “one time observable” (1TO), or more precisely the ones that can be written as sum of local quantities, are close to equilibrium. We call this situation *ultra-long time limit* and observe that in principle a) this limit does not imply the absence of aging in two time observables such as responses and correlation functions, b) usual nucleation arguments imply that in systems with regular short range interactions this limit is achieved in a finite, i.e. volume independent, time. Of course this last observation remains a matter of principle in structural glasses, where this equilibration time is exceedingly long, and one needs to understand dynamics on much shorter time scale.

For notational simplicity, in the theory we are going to expose, we will use the language of magnetic systems. Our considerations however will very general and can immediately applied e.g. to glass forming systems of classical

particles in interaction. In order to illustrate the ideas we discuss a spin glass system where the spins  $S_x$  interact through a Hamiltonian

$$H(\mathbf{S}) = - \sum_{\mathbf{x} < \mathbf{y}} \mathbf{J}_{\mathbf{x},\mathbf{y}} \mathbf{S}_{\mathbf{x}} \mathbf{S}_{\mathbf{y}}. \quad (1)$$

on the D-dimensional square lattice and short range interactions  $J_{x,y}$ . The spins will be for simplicity assumed to be Ising variables  $S_x = \pm 1$ . We will consider the dynamical setting of a fast quench from high to low temperature at an instant marking the origin of the time axes.

## II. AGING IN THE ULTRA-LONG TIME LIMIT

The classical aging experiments concentrate on the study of the response of the system to an external perturbation in the linear regime. Consider the effect of an external magnetic field  $h$ , corresponding to a perturbation term in the Hamiltonian  $H^{(1)}(\mathbf{S}) = -h \sum_{\mathbf{x}} \mathbf{S}_{\mathbf{x}}$ , acting from the quenching time 0 to a waiting time  $t_w$ . At the linear order in  $h$ , the magnetization  $M(t, t_w) = \frac{1}{N} \sum_{\mathbf{x}} \langle S_{\mathbf{x}}(t) \rangle_h$  at later times  $t$  can be written as  $M(t, t_w) = h \chi(t, t_w)$ , where, introducing the instantaneous response  $R(t, s) = \frac{\delta \langle M(t) \rangle}{\delta h(s)}$ , the susceptibility can be written as  $\chi(t, t_w) = \int_0^{t_w} ds R(t, s)$ . This is a quantity usually measured in aging experiments and exhibit scaling, non-time translation invariant behavior. In usual equilibrium regimes, this function is related to the correlation function  $C(t, t_w) = \frac{1}{N} \sum_{\mathbf{x}, \mathbf{y}} \langle S_{\mathbf{x}}(t) S_{\mathbf{y}}(t_w) \rangle$  by the fluctuation-dissipation relation  $\chi(t - t_w) = \beta C(t - t_w)$ . Off-equilibrium the same relation has in general no reason to be valid. One usually defines the fluctuation-dissipation ratio (FDR)

$$\beta \tilde{x}(t, t_w) = \frac{\partial \chi(t, t_w) / \partial t_w}{\partial C(t, t_w) / \partial t_w} \quad (2)$$

or  $x(t, C)$  defined by the relation  $x(t, C(t, t_w)) = \tilde{x}(t, t_w)$ . In equilibrium conditions the FDR is equal to unity and  $\chi(t, t_w) = \beta C(t - t_w)$ . Spin glass mean field theory [3–5], has suggested that in aging systems  $x(t, C)$  tends to a non trivial limit  $x(C)$  taking the limit  $t, s \rightarrow \infty$  for fixed values of  $C(t, s)$ . In these systems the FDR appears to have some universal character. It is independent of the particular response/correlation function probed. The function  $x(C)$  appears to have mathematically the properties of a probability function. The ratio  $T/x(C)$  can be considered an effective temperature governing heat exchanges on degrees of freedom reacting on the time scales specified by the value of the correlation [11]. Such non generic behavior can be understood in the ultra-long time limit, resulting in a rather detailed statistical description on how glassy systems visit configurational space in aging dynamics. In the limit in which the FDR becomes time independent, one time observables (e.g. energy and magnetization) become asymptotically close to their final value. We will call this limit “ultra-long time limit” in reference to the fact that structural glasses are always observed on much shorter time scales. Let us stress that in short range systems with regular interactions the asymptotic values of the 1TO must be the equilibrium one. The ultra-long time limit while it could be appropriate in spin glasses where the values of 1TO’s seem not to depend on cooling procedure, but it is certainly not an appropriate description for structural glasses, where the 1TO are strongly out of equilibrium. In this context we can still think of this limit as a useful conceptualization to study aging in a simplified situation and getting hints on the statistical principles that govern glassy dynamics even far from this ideal situation.

## III. EQUILIBRIUM ERGODICITY BREAKING

We would like to discuss how a non trivial FDR in the ultra-long time limit relates to the phenomenon of ergodicity breaking in the equilibrium distribution. Breaking of ergodicity, or absence of ergodicity at equilibrium means that the weight of the equilibrium distribution is concentrated on more then one disjoint phase space regions, called ergodic component, where the ergodic property holds separately. If the system is prepared in one of these regions it will never get out from it. A familiar example is provided by systems in presence of a first order phase transition, where different phases are equally dynamically stable. In that case suitable “external field” can be used to project on the different phases. The situation we would like to describe, that of an ideal glass, can be expected to be different. In disordered systems, the possible different ergodic components dominating at low temperature can be expected to be as disordered as the configurations of the high temperature phase and no external field is available to select any of them. A suitable description of that situation has been provided by spin glass mean field theory [18] where ergodicity breaking is characterized statistically through the comparison of the different ergodic components. One first define

a measure of similarity among configuration, and then studies its statistical distribution induced by the canonical measure and the eventual quenched disorder. For spin glasses it is natural to define the overlap between two spin configurations  $\mathbf{S} = (S_1, \dots, S_N)$  and  $\mathbf{S}' = (S'_1, \dots, S'_N)$  as the normalized scalar product:

$$q(\mathbf{S}, \mathbf{S}') = \frac{1}{N} \sum_i S_i S'_i \quad (3)$$

The overlap probability function (OPF), is defined as

$$P(q) = \overline{\frac{1}{Z^2} \sum_{\mathbf{S}, \mathbf{S}'} \exp(-\beta(H(\mathbf{S}) + H(\mathbf{S}')) \delta(q - q(\mathbf{S}, \mathbf{S}'))}. \quad (4)$$

where the over-line denotes the average over the quenched variables of the system (if any). If ergodicity holds the OPF equal to a single delta function. Any difference from this simple form is sign of ergodicity breaking. Conversely, a single delta function is not necessarily associated to ergodicity. The different components  $\alpha = 1, 2, 3, \dots$  appear in the equilibrium distribution each with a probability weight  $w_\alpha$  reflecting its free-energy difference with the lowest state. It turns out that the OPF can be non-trivial only if the participation ratio  $\sum_\alpha w_\alpha^2$  is non-vanishing in the thermodynamic limit. This excludes e.g. the case of an extensive number of ergodic component where  $w_\alpha \sim \exp(-N\Sigma)$ .

Despite its origin in the context of spin glasses, the concept of overlap, and the corresponding probability function, can be suitably to more general glassy systems. A possible definition in the case of structural glasses and some applications are discussed in [19,20].

#### IV. HOW AGING RELATES TO EQUILIBRIUM

Linear response theory allows to relate the OPF of the canonical probability and the FDR according to the relation [12]:

$$P(q) = \frac{dx(q)}{dq}. \quad (5)$$

The argument that leads to (5) is rather formal, and consists in finding a family of observables, expressed as sum of local quantities, whose average values relate respectively in equilibrium and in dynamics to the moments of the OPF and the derivative of FDR with respect to the correlation. As the dynamical averages should tend to the equilibrium ones, one deduces the identity between the OPF and the derivative of the FDR. The arguments runs as follow. Let us consider a set of operators which translate the lattice along a direction  $\hat{i}$  parallel to one of the coordinate axes:

$$\mathcal{T}_k^{(p)}(x) = x + \frac{kL}{p} \hat{i}; \quad k = 1, \dots, p-1. \quad (6)$$

We denote by  $\mathcal{S}_1$  the set in which the coordinate in the direction  $\hat{i}$  takes the values  $1, 2, \dots, L/p$ . We define our family of perturbations to have the form

$$H_p(\mathbf{S}) = \sum_{x \in \mathcal{S}_1} J_x^{(p)} S_x S_{\mathcal{T}_1^{(p)}(x)} \cdots S_{\mathcal{T}_{p-1}^{(p)}(x)}, \quad (7)$$

where the couplings  $J_x^{(p)}$  are independent, identically distributed Gaussian variables, with zero mean and variance  $E_J J_x^2 = p$ . Despite the apparent long range character of the interactions, the perturbations  $H_p$  can be seen as short range observable in a folded space, and as such they belong to the class of observables whose long time limit values tend according to our hypothesis to the equilibrium ones. Let us consider now a system evolving with Hamiltonian  $H + hH_p$ . These perturbations can be seen as short range perturbation and one can expect their effect to be described by linear response theory for small  $h$ . If we consider the expected values, in off-equilibrium dynamics and at equilibrium of the perturbation  $H_p$ , following simple mathematical manipulations implied by linear response theory and by self-averaging properties with respect to the variables  $J_x^{(p)}$ , one finds respectively for the dynamic and equilibrium averages

$$\langle H_p(t) \rangle_{dyn} = -\beta h \int_0^1 dq p q^{p-1} x(t, q) \quad (8)$$

$$\langle H_p \rangle_{eq} = -\beta h (1 - \int_0^1 dq q^p P(q)) \quad (9)$$

In the ultra-long time limit,  $\langle H_p(t) \rangle_{dyn} \rightarrow \langle H_p \rangle_{eq}$  for all  $p$ . Correspondingly,  $x(t, q) \rightarrow x(q)$  and integrating (8) by parts we find the relation (5). This relation relates the possibility of a persistent non-trivial FDR in the aging dynamics to ergodicity breaking in the equilibrium measure, and as we will discuss, can be taken as the starting point for an analysis of how aging systems visit configuration space. The relation can be generalized to other important features which have been identified theoretically as possible in aging dynamics. One of this feature is ultrametricity which at equilibrium implies a hierarchical organization of the ergodic components. In dynamics this property means that the times  $t(C, t_w)$  necessary for the correlation  $C(t, t_w)$  to take the value  $C$  and defined by the relation  $C(t(C, t_w), t_w) = C$  verify for  $C_1 < C_2$  the relation:  $t(C_2, t_w)/t(C_1, t_w) \xrightarrow{t_w \rightarrow \infty} 0$ , in other words that decreasing values of the correlation correspond to increasingly long relaxation times. Reasoning similar to the ones that lead to (5) allow to conclude that surprisingly in a given systems static ultrametricity and dynamic ultrametricity either are both present or both absent. Recently the relation (5) has also been generalized to local quantities in [21]. A more complete discussion of the relation (5) should qualify the validity of the use of linear response in presence of ergodicity breaking, which involves the commutation of the thermodynamic limit and  $h \rightarrow 0$  in statics, as well as the long time limit and  $h \rightarrow 0$  in dynamics. This property has been called “stochastic stability”, in reference to the fact that the commutation of limits is possible whenever the introduction of weak random perturbations of the kind (7) has not major effects on the statistical distribution of the states relevant for the equilibrium probability and the long time off-equilibrium dynamics. On physical ground one expects stochastic stability to be valid and linear response theory to have a range of validity in glassy systems. Violation of this properties should result in dynamical crossovers for  $t \rightarrow \infty$  and  $h \rightarrow 0$  which are in principle experimentally observable. So if in some systems one could measure the asymptotic value of the FDR this would lead informations on the equilibrium free-energy landscape.

## V. PHYSICAL PICTURE

The relation (5), which links off-equilibrium dynamics to the properties of the free-energy landscape relevant at equilibrium, has been discussed in the previous section on a purely formal ground: we have supposed equilibration of 1TO together validity of LRT and obtained the relation from straight mathematical analysis. The scope of this section is to discuss its physical origin. In order to simplify the discussion, we will consider the simplest model of aging dynamics with a non-trivial FDR. We will suppose that the dynamics will consists in a short time equilibrium like part and a long time aging part characterized by a unique age dependent relaxation time  $\tau(t_w)$  which grows and tends to infinity for large  $t_w$ . Notice that this is the assumption commonly used to fit aging response data both in structural glasses [1] and in spin glasses [2]. In this picture the correlation functions can be decomposed in a stationary short time part and an aging long time part as

$$C(t, t_w) = C_{st}(t - t_w) + C_{ag} \left( \frac{t - t_w}{\tau(t_w)} \right) \quad (10)$$

as usual we define  $q_{EA}$  as the value that separate the stationary from the aging part of the correlation so that  $C_{st}(t - t_w) = C_{st}^*(t - t_w) - q_{EA}$  is a monotonically decreasing function equal to  $1 - q_{EA}$  for  $t - t_w = 0$  and tending to zero for  $t - t_w \rightarrow \infty$ , while  $C_{ag}(\frac{t - t_w}{\tau(t_w)})$  is equal to  $q_{EA}$  for  $\frac{t - t_w}{\tau(t_w)} = 0$  and tends to 0 for  $\frac{t - t_w}{\tau(t_w)} \rightarrow \infty$ . Correspondingly we will assume that the FDR will take the value 1 in the stationary domain ( $q_{EA} \leq C(t, t_w) \leq 1$ ) and the constant value  $x < 1$  in the aging regime  $C(t, t_w) \leq q_{EA}$ , so that the linear susceptibility takes the form

$$\chi(t, t_w) = \beta C_{st}(t - t_w) + \beta x C_{ag} \left( \frac{t - t_w}{\tau(t_w)} \right) \quad (11)$$

. The relation between correlation and response is often visualized plotting parametrically  $\chi(t, t_w)$  vs.  $C(t, t_w)$  for fixed  $t_w$ . The present case corresponds to having for large  $t_w$  two straight lines respectively of slope  $\beta$  for  $q_{EA} < C(t, t_w) \leq 1$  and  $\beta x$  for  $0 \leq C(t, t_w) < q_{EA}$ . This form of the correlation and response is the one found in models of the  $p$ -spin model family [3]. Numerical simulations of glass-forming systems indicate that the two regime behavior is a good approximation for the finite  $t_w$  behavior of the response not too close to the estimated value of  $q_{EA}$ , although in that case the parameter  $x$  depends on  $t_w$  [22]. In these cases however 1TO are far from equilibrium, differently from what we suppose here.

The form (11) corresponds to an equilibrium distribution where the function  $P(q)$  has the simple form

$$P(q) = (1 - x)\delta(q - q_{EA}) + x\delta(q). \quad (12)$$

A straightforward computation shows that the observables  $H_p$  of the previous section are expressed according to (9) as

$$\langle H_p \rangle = -\beta h(1 - q_{EA}^p + x q_{EA}^p). \quad (13)$$

The equilibrium regime at short times implies that the system spends its time in regions of the configuration space where it has the time of approximately equilibrate before relaxing further on a much longer scale. This observation can be put at the basis of decomposition where the dynamical variables, say the instantaneous values of the spins, are written as the sum of a fast and a slow contribution.

$$S_x(t) = [S_x(t) - m_x(t)] + m_x(t), \quad (14)$$

where  $[S_x(t) - m_x(t)]$  is the fast component and the slow component  $m_x(t)$  can be simply defined as

$$m_x(t) = \frac{1}{\tau(t_w)} \int_t^{t+\tau(t_w)} du S_x(u). \quad (15)$$

The set of the fast variables that correspond to the same slow variables define metastable regions of configuration space, called “quasi-states” that have a life time of the order of  $\tau(t_w)$ . This notion can be related to the potential energy landscape notions of basin or more precisely metabasins [23] in the inherent structure picture [24], with whom the quasi-states could be identified.

We can at this point rather naturally define thermodynamic quantities: to each quasi-state labeled by the values of the slow variables  $\mathbf{m} = (m_1, \dots, m_N)$  we can associate a free-energy  $f(\mathbf{m})$  and we can define a “configurational entropy”  $\Sigma(f)$  as the logarithmic multiplicity of quasi-states as a function of their free-energy  $f$ .

For long but finite times the quasi-states dominating the dynamics will present a small but extensive free-energy difference with the lowest state. The parameter  $q_{EA}$  has the meaning of self-overlap within a quasi-state:  $q_{EA} = \frac{1}{N} \sum_x m_x^2(t)$ . The equilibrium distribution on the other hand concentrates on the ergodic components, or true states, which have finite free-energy differences with the ground state and infinite life time. As we have stressed, if the function  $P(q)$  is non trivial the multiplicity of such states grows less then exponentially with  $N$ . On the other hand, for the number of quasi-states with free-energy difference  $N\Delta f$  with the ground state, one can expect:  $\mathcal{N}(f) \sim \exp(N\rho\Delta f)$ .

Let us discuss the effect on the system of a small perturbation and concentrate for simplicity on the case of  $p = 1$ , corresponding to an external magnetic field. As discussed first in [25], the effect of the field on the equilibrium distribution will be twofold. On one hand within any given ergodic component, with given average magnetization  $M_{av}$ , higher weight will be given to configurations with higher magnetization difference with the average  $M - M_{av}$ . On the other, in the selection of the components higher weight will be given to components with higher average magnetization. The actual value the magnetization will take can be then understood as a two step free-energy minimization process. The first step is a single component free-energy minimization. This is done according to the usual equilibrium relation within a component  $\beta h(M - M_{av}) = \frac{1}{N} \beta [\langle H_1^2 \rangle_{s.c.} - \langle H_1 \rangle_{s.c.}^2] = -\beta h(1 - q_{EA})$ , where with  $\langle \cdot \rangle_{s.c.}$  we have denoted the average on a single component. The second step is the choice of the components with the appropriate average magnetization. The probability that a given unperturbed component has average magnetization  $M_{av}$  is for small values of  $M_{av}$  Gaussian with zero average and variance  $Nq_{EA}$ . Taking then into account the independence of the perturbation from the original Hamiltonian, we have that the number of quasi-states with free-energy difference  $\Delta f$  with respect to the unperturbed ground state and average magnetization  $M_{av}$  is given by

$$\mathcal{N}(f, M_{av}) \sim \exp(N[\rho\Delta f - M_{av}^2/2q_{EA}]) \quad (16)$$

In presence of the perturbation the actual value of  $M_{av}$  will be that one minimizing  $\Delta f - hM_{av}$ , respecting the constraint that the number of states is higher then zero:  $\rho\Delta f - m^2/2(1 - q_{EA}) \geq 0$ . One finds that the minimization is achieved in fact for  $\rho\Delta f - M_{av}^2/2(1 - q^p) = 0$  thus finding, comparing with (13) that  $\rho = \beta x$ .

The equivalence (9) tells that the same selection criteria should be valid asymptotically in off-equilibrium dynamics. The way the energy distributes among the different degrees of freedom in dynamics is asymptotically the same as at equilibrium. Free-energy not only governs equilibrium, but also dynamics: quasi-states of equal free-energy are selected asymptotically with equal probability. Notice that this conclusion do not depend on the observables we have considered in the analysis, according to our line of reasoning the same factor  $x$  appears in the anomalous response to any perturbation. Under these circumstances one may wonder how the system can always be microscopically far from the true equilibrium components as the off-equilibrium behavior of correlation and response implies. This relates to the abundance of quasi-states extensive the free-energy difference  $N\Delta f$ , which in order to have a non trivial FDR must be exponentially large. In that case a small  $\Delta f$  while implies small difference for the 1TO from the equilibrium values, it implies big microscopic differences between the quasi-states visited and the ergodic components.

This considerations, based on time scale separation and vicinity of 1TO to their equilibrium value does not of course directly apply to structural glasses. However, based on the analysis of the case of the  $p$ -spin model where 1TO block to values different from the equilibrium ones [13] one can hypothesize that the previous quasi-state selection principle

could also be valid far from the ultra-long time limit. This is comforted by numerical simulations which have reported the existence of well defined FDR very far from equilibrium which are fairly constant on the aging regime [22] and do not appear to depend on different quantities which have been studied [26].

In this regime we probe in a region of parameters corresponding to finite configurational entropy, and as 1TO are strongly out of equilibrium, no connection can be made between the measurable values of the FDR and the equilibrium OPF. However, thanks to equiprobability also in this case the FDR can be related to some static characterization of the configuration space. At a given time, corresponding to a quasi-state free-energy  $f$  the system will have reached with equal probability one of the  $\mathcal{N}(f) \sim \exp(N\Sigma(f))$  possible quasi-states, where the configurational entropy  $\Sigma(f)$  is an increasing function of  $f$ . In order to rationalize the relation (13) one has just to suppose that the dynamics is dominated by the relaxation of the configurational entropy towards smaller values, and that a small perturbation in the Hamiltonian do not change its rate of reduction. In other words, at a given time  $t_w$ , the configurational entropy will take the same value  $\Sigma(t_w)$  both in absence and in presence of the perturbation. Writing then the total free-energy as an unperturbed term  $f$  plus a perturbation term  $-\beta h M_{av}$  one can write that  $\Sigma(t_w) = \Sigma(f) - M_{av}^2/2(1 - q_{EA})$ . Minimizing the total free-energy  $f = f - \beta h M_{av}$  with this constraint one recovers the formula (13) with the relation

$$\beta x = \frac{\partial \Sigma}{\partial f} \quad (17)$$

during aging the effective temperature  $1/(\beta x)$  verifies with the configurational entropy the same relation that the true temperature verifies at equilibrium with the total thermodynamic entropy. This kind of relation has been recently used to argue in favor of the “Edwards measure” for lattice gas systems [16] and granular material under shear [27]. Let us notice that even if this is not indicated explicitly in the notation, now the various parameters ( $f$ ,  $q_{EA}$  etc.) are slow functions of time. The equiprobability hypothesis, if in the ultra-long time limit it comes rather naturally from 1TO equilibration, is much harder to justify in when these quantities are out of equilibrium. At present they are not clear the physical principles that would explain it, although it has been tentatively related to a chaotic property with respect to the thermal noise [28] according to which two “clones”, generated doubling a given system at the time  $t_w$  and evolving later with different realization of the thermal noise, would give rise to divergent trajectories.

We would like to stress that the analysis we have presented implies equivalence between the relaxation of field induced perturbations after removal of the field and the regression of spontaneous fluctuation [13] in a way that generalizes the classical Onsager argument for equilibrium systems [29]. Both kind of conditions in fact imply free-energy minimization with a configurational entropy constraint, and within the two step relaxation model we have considered lead to the relation (11).

Up to now we have considered as a reference setting a simple quench from high to low temperature. We can generalize the present dynamical picture to more complex thermal histories retaining equiprobability of quasi-states with equal free-energy. We would get in this case a dynamical picture in agreement with multi-temperature thermodynamics described in [30], where the macroscopic state of a glass is specified by a suitable number of history dependent effective temperatures. The model discussed here corresponds to just an effective temperature in addition to the external one. According to direct numerical measurement of the FDR in glass-forming models this corresponds to a good approximation to the situation found in model liquid systems [22]. Good indications in favor of the present picture come from numerical simulations of glass forming liquids. In ref. [31] the relation (17) has been tested with positive answer starting from a direct measure of the FDR and an estimate of the configurational entropy as the logarithmic number of inherent structure with given energy. Other interesting numerical evidence has been found in the Kob-Andersen kinetic model in [16] and in the related problem of granular materials under shear in [27]. Experimentally there are clear evidence that violations of FDT are present on long time scales [8–10], but if these correspond to effective temperatures is not clear at the present stage.

## VI. CONCLUSIONS

In this paper we have discussed a possible picture on how glassy system visit configuration space based on the analysis of the fluctuation dissipation relations during aging. The ultra-long time limit, possibly relevant for the case of spin glasses, gives us a case where we can understand in a good detail the meaning of anomalous response and effective temperatures defined from off-equilibrium fluctuation dissipation relations. The asymptotic value of anomalous response is related to the existence of a non trivial equilibrium OPF  $P(q)$ , which in turn implies ergodicity breaking in the equilibrium distribution. The meaning of the equivalence can be found in a dynamical principle of selection of the quasi-states in the asymptotic limit: quasi-states with equal free-energy are selected with equal probability in the dynamical process. Under these circumstances where the system is macroscopically close to equilibrium, the

possibility of always being microscopically far from equilibrium and continue to age relates to the abundance of states, which in order to have a non trivial FDR must be exponentially large as soon in the free-energy difference  $\Delta f$  is finite.

This leads to a dynamical picture that can be generalized to the case in which the system is macroscopically out of equilibrium, assuming equiprobability of quasi-states of equal free-energy, and a rate of decrease of the configurational entropy independent of possible small perturbations. This hypothesis predicts the existence of FDR (effective temperatures) related to the growth of the configurational entropy with quasi-state free-energy and therefore independent of the particular couple of correlation and response measured. The experimental verification of this property, and the clarification of the physical principles leading to it are open problems for future research.

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